# WEEKEND/WEEKDAY OZONE OBSERVATIONS IN THE SOUTH COAST AIR BASIN: RETROSPECTIVE ANALYSIS OF AMBIENT AND EMISSIONS DATA AND REFINEMENT OF HYPOTHESES

Volume I – Executive Summary

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Prepared for

NATIONAL RENEWABLE ENERGY LABORATORY
1617 Cole Boulevard
Golden, CO 80401-3393

Prepared by

Eric M. Fujita, William Stockwell, Robert E. Keislar, and David E. Campbell
Desert Research Institute
2215 Raggio Parkway
Reno, NV 89512

Paul T. Roberts, Tami H. Funk, Clinton P. McDonald, Hilary H. Main, and Lyle R. Chinkin
Sonoma Technology, Inc.
1360 Redwood Way, Suite C
Petaluma, CA 94954-1169

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## TABLE OF CONTENTS


Section — Page No.

Acknowledgment ..... ii
Table of Contents ..... iii
List of Tables ..... iv
List of Figures ..... iv

1. INTRODUCTION ..... 1

2. PROJECT OBJECTIVES AND SCOPE ..... 2

3. STUDY RESULTS ..... 4
- 3.1 Analysis of Ambient Data ..... 4
- 3.2 Summary of Available Emissions Data ..... 11
- 3.3 Review of Source Apportionment Analyses ..... 14
- 3.4 Analysis of SCOS97-NARSTO Meteorological and 3-D Ozone Data ..... 15

4. PRELIMINARY CONCEPTUAL EXPLANATION OF THE "WEEKEND EFFECT" ..... 17

5. PHASE II PLAN ..... 22
- 5.1 Selection of Hypotheses for Phase 2 ..... 22
- 5.2 Data Analysis Approach ..... 24
- 5.3 Phase II Measurement Plan ..... 25
- 5.4 Emission Inventory Development ..... 28
- 5.5 Meteorological And Aloft Air Quality Analysis Plan ..... 29
- 5.6 Schedule ..... 29

6. REFERENCES ..... 30

## LIST OF TABLES


| Table No. | | Page No. |
|---|---|---|
| Table 1 | Trends in duration and rate of ozone accumulation in the SoCAB, 1981-1999 | 7 |
| Table 2 | 1996 average daily emissions in the SoCAB (California Air Resources Board, 1998). | 10 |


## LIST OF FIGURES


| Figure No. | | Page No. |
|---|---|---|
| Figure 1 | Average summer 1995 diurnal variations of $O_3$, NO, $NO_2$, and CO at Azusa during weekday and weekend | 5 |
| Figure 2 | Average summer 1995 diurnal variations of $O_3$ and VOC/NOx at Azusa during weekday and weekend. | 6 |
| Figure 3 | Sunday versus Wednesday differences in duration and rate of ozone accumulation for twelve sites in the SoCAB during 1981-84, 1985-89, 1990-94, and 1995-98... | 8 |
| Figure 4 | Trends in average maximum 1-hour ozone from 1980 to 1997 in the western, central and eastern portions of the South Coast Air Basin... | 9 |
| Figure 5 | Sunday minus Wednesday differences in the duration and rates of ozone accumulation for the years 1981-84, 1985-1989, 1990-1994, and 1995-1998 | 10 |
| Figure 6 | Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized as VOC- or NOx-limited | 19 |
| Figure 7 | Sampling locations during the Phase II field study | 27 |
| Figure 8 | Residential survey form for small point and area sources | 29 |

# 1. INTRODUCTION

Since the mid-1970s it has been documented that ozone ($O_3$) levels in California's South Coast Air Basin are higher on weekends than on weekdays, in spite of the fact that ozone pollutant precursors are lower on weekends than on weekdays (Elkus and Wilson, 1977; Horie et al., 1979; Levitt and Chock, 1976; Zeldin et al., 1989; Blier et al., 1996; Blier et al., 1999; and Austin and Tran, 1999). Similar effects have been observed in San Francisco (Altshuler et al. 1995) and the northeastern cities of Washington D.C., Philadelphia, and New York (SAIC, 1997). While a substantial weekend (WE) effect has been observed in these cities, the effect is less pronounced in Sacramento (Austin and Tran, 1999), and is often reversed in Atlanta (Walker, 1993) where VOC/NOx ratios are typically higher.

The Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) are conducting a study of the causes of elevated ozone levels on weekends in the South Coast (Los Angeles) Air Basin (SoCAB). The work is being conducted in three phases over a period of 30 months. In Phase I, a retrospective analysis of existing ambient air quality and meteorological data for the South Coast Air Basin is intended to improve the current conceptual understanding of the physical and chemical processes that drive the "weekend effect" and to refine the hypotheses that will be addressed by this study. In Phase II, a field measurement program will be conducted during summer-fall 2000 to collect and assemble air quality and emission activity databases to test our hypotheses. The data analyses during Phase III may include temporal and spatial variations in ozone, ozone precursors, and emission source indicators (e.g., carbon monoxide [CO], nitric oxide [NO], total and speciated non-methane hydrocarbons [NMHC], and elemental carbon [EC]), time-resolved hydrocarbon source apportionment, analysis of emissions activity data, evaluation of the weekend effect by semi-empirical methods and review of air quality model simulations of Southern California Ozone Study (SCOS97-NARSTO) episodes. The results of these analyses will be reconciled with the current understanding of the WE ozone effect in the SoCAB.

This report summarizes the analysis of available air quality and emissions inventory data during Phase I of the study. This Phase of the study is supported by the National Renewable Energy Laboratory (NREL) and Phases II and III are supported by NREL and the Coordinating Research Council. Phase I is being conducted in coordination with the Weekend Effect Workgroup sponsored by the California Air Resources Board (ARB).

## 2. PROJECT OBJECTIVES AND SCOPE

The overall objectives of Phase I are to acquire emissions activity data, meteorological data, and air quality data and to analyze these data to establish data needs and priorities during the Phase II field study. The following tasks were carried out by DRI and STI during Phase I of the study.

DRI Task 1: Analyze retrospective ozone and ozone precursors. Assemble an air quality database for ozone, carbon monoxide, total non-methane hydrocarbons and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. From the current conceptual explanations of the weekend effect, identify key air quality parameters and their spatial, temporal and statistical distributions that can be used to gain further insight into the weekend effect.

STI Task 1: Review available emissions data. Based on available emission inventory data, identify VOC and NOx sources with the potential to be different on weekends than on weekdays. Summarize the diurnal variations in daily VOC and NOx emissions by day-of-the-week for these sources. Review the method(s) used to determine temporal variations and evaluate uncertainties and identify alternative methods or additional data that are available to update and improve existing temporal allocation of VOC and NOx emissions.

DRI Task 2: Review source apportionment analyses. Review the source apportionment analysis conducted by the Desert Research Institute for the SoCAB and characterize the day-of-the-week variations in source contributions. Review available source composition profiles and identify sources for which updated profiles are needed.

STI Task 2: Analyze SCOS97-NARSTO meteorological and 3-D ozone data. Evaluate meteorological conditions during SCOS97-NARSTO intensive operational periods (IOPs) to determine applicability of each weekend and weekday IOP for assessments of the WE effect. For applicable IOPs, characterize the surface and aloft spatial and temporal patterns of ozone and ozone precursors utilizing the aloft ozone data measured by LIDAR and instruments on aircraft. Compare the results to 1987 IOPs and determine if the patterns are similar or different. Compare the 1997 weekend and weekday IOPs. Investigate the influence of the mixing heights and wind patterns on ozone concentrations during applicable weekend and weekday IOP days. Determine if any of the SCOS97 weekend and weekday IOPs are meteorologically similar in terms of mixing heights, winds, 850 mb temperature, ARB flow type, and synoptic pattern. Develop a matrix of meteorological similarities and differences for the IOP days. Compare the surface and aloft spatial and temporal patterns of ozone and ozone precursors on the IOPs and conceptually quantify the variation in ozone patterns between the weekend and weekday IOP days based on the meteorology. For applicable IOPs, analyze the data from the SCOS97 upper-air meteorological network and evaluate the regional representativeness of the temporal and spatial variations in wind and mixing heights that can be obtained from the two PAMS profilers (at LAX and Ontario) alone.

DRI and STI Task 3: Synthesize Phase I data analysis and prepare Phase 1 Report. Summarize the results of the Phase I data analysis. Compare results from each task. Update hypotheses. Revise the conceptual model. Finalize the field measurement program.

The results of Task 3 for DRI and STI are presented in this Executive Summary (Volume I). A preliminary conceptual explanation of the "weekend effect" is derived from an integration of the retrospective analyses of air quality, emission inventory and meteorological data. Alternative hypotheses for the WE effect are considered with respect to this preliminary conceptual explanation, and experimental approaches are proposed for the Phase II field study in the fall 2000 and subsequent Phase III data analysis to evaluate these hypotheses. Results of Tasks 1 and 2 for DRI and STI are documented in Volume II (Fujita et al., 2000) and Volume III (Roberts et al., 2000), respectively.

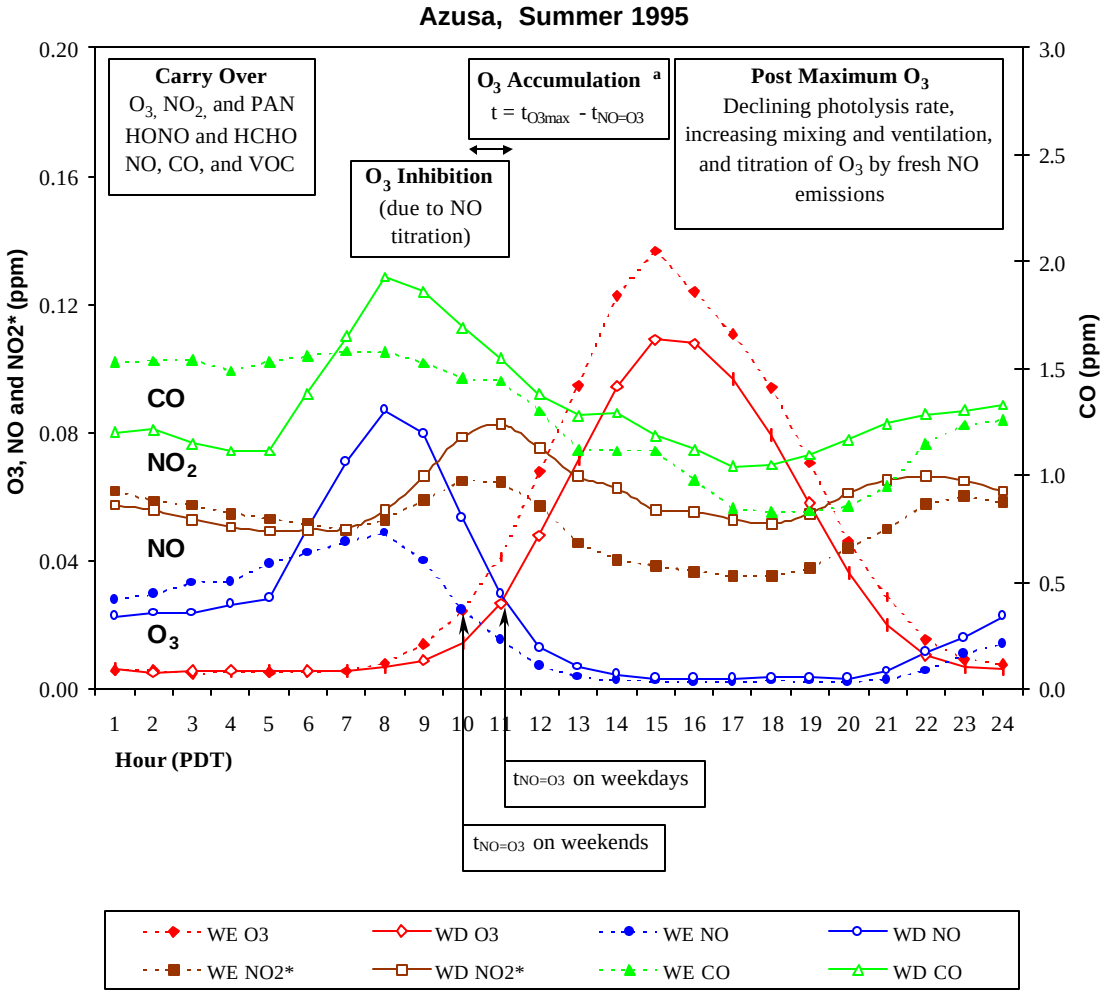
# 3. STUDY RESULTS

The key findings of the retrospective analysis of emissions, ambient pollutant and meteorological data are summarized below.

## 3.1 Analysis of Ambient Data

The average maximum 1-hour ozone concentrations by day-of-the-week for twelve sites in the Basin show that the weekend effect has changed significantly during the period from 1981 to 1999. In the period 1981-84, ozone levels were higher on weekdays in most of the central and eastern portions of the basin. Most monitoring sites in the western basin showed slightly higher weekend ozone concentrations. The weekend effect remained relatively weak during 1985-89 with a pronounced dip in ozone concentrations on Mondays. Weekend ozone values were not statistically different from Tuesday-Friday values at most sites in the central and eastern basin. By 1990-94, ozone concentrations were higher on weekend throughout the basin and the weekend effect continued to strengthen during 1995-98. The average Sunday/Wednesday ozone ratios for all twelve sites for the periods 1981-84, 1985-89, 1990-94, and 1995-98 were 1.00, 1.02, 1.18 and 1.26, respectively. The corresponding Saturday/Wednesday ozone ratios were 1.03, 1.04, 1.17, and 1.24, respectively. Larger reductions in peak ozone concentrations have occurred on weekdays. Ozone concentrations in 1995-98 expressed as ratios of the 1981-84 values range from 0.54 to 0.59 on Monday through Friday, 0.67 on Saturday, and 0.70 on Sunday. The differences among the twelve sites in average peak 1-hour ozone are significantly smaller now than in years past due to larger reductions in the central portion of the basin.

The diurnal ozone cycle consists of four phases: overnight carryover of ozone precursors; inhibition of ozone formation during the morning due to titration with NO; accumulation of ozone from the end of the inhibition period to the time ozone reaches its maximum; and post ozone maximum, which is characterized by increased vertical mixing and horizontal advection, declining actinic flux, and titration of ozone by fresh NO emissions during the afternoon. Figure 1 shows the average diurnal variations of $O_3$, NO, $NO_2$, and CO at Azusa for summer 1995. During the ozone inhibition period, formaldehyde (HCHO) and, to a lesser extent, nitrous acid (HONO) are the main sources of HO radicals. We used the time in the morning when NO and $O_3$ cross over (i.e., $t_{NO=O3}$) as a marker for the end of the inhibition period and the beginning of $O_3$ production via conversion of NO to $NO_2$ by peroxy radical. The crossover, and thus the start of ozone formation, occurs earlier on weekends. Another factor in the WE effect is the faster rate of ozone accumulation on weekends relative to weekdays. Duration of ozone accumulation was estimated by the difference between time of maximum ozone ($t_{maxO3}$) and $t_{NO=O3}$. The rate of ozone accumulation (ppb/hour) is the increase in ozone from $t_{NO=O3}$ to $t_{maxO3}$ divided by the duration of ozone accumulation. Ozone is higher on weekends at Azusa because the duration of ozone accumulation is longer and the rate of ozone accumulation is faster. Figure 2 shows that VOC/NOx ratios are higher during weekends, which could explain the higher rate of ozone formation. These parameters are examined for twelve sites in the SoCAB for the years 1981 to 1999.




a. O3 accumulation rate = [O3(max) - O3 ($t_{NO=O3}$)]/($t_{O3max}$ - $t_{NO=O3}$)

Figure 1. Average summer 1995 diurnal variations of $O_3$, NO, $NO_2$, and CO at Azusa during weekday and weekend. The shorter ozone inhibition period and higher rate of ozone formation are the main factors causing higher ozone on weekends.

The overnight carryover of NO is lower on Sunday and Monday mornings and higher at the end of the week on Friday and Saturday. NO carryover is 10-20 percent lower on Sunday and Monday relative to midweek and about 10-15 percent higher on Friday and Saturday mornings. Note that pollutant concentration values shown at 0100 are very different from those at 2400 for CO and NO on weekends. This is because the carryover averaged for Friday and Saturday is greater that the carryover averaged for Saturday and Sunday. Overnight carryover of NMHC is greatest on Saturday and Sunday mornings with ratios to Wednesday of 1.20 and 1.12, respectively, and least on Monday mornings. Higher carryover of NMHC on Sunday relative to Wednesday coupled with lower relative carry-over of NO suggests that the carryover of NO and NMHC emissions is driven by different sources. $NO_2$ shows no significant day-of-the-week differences. The magnitude of the carryover of NO and $NO_2$ has decreased about 20 percent over the past 18 years. The fraction of NOx that is $NO_2$ ranges from 60 to 90 percent with lowest

fractions at Los Angeles–N. Main, Pico Rivera, Burbank and Pomona and highest fractions at N. Long Beach, Anaheim, and Upland. There are no significant day-of-the-week variations in the $NO_2$/NOx ratios during the overnight carryover period.

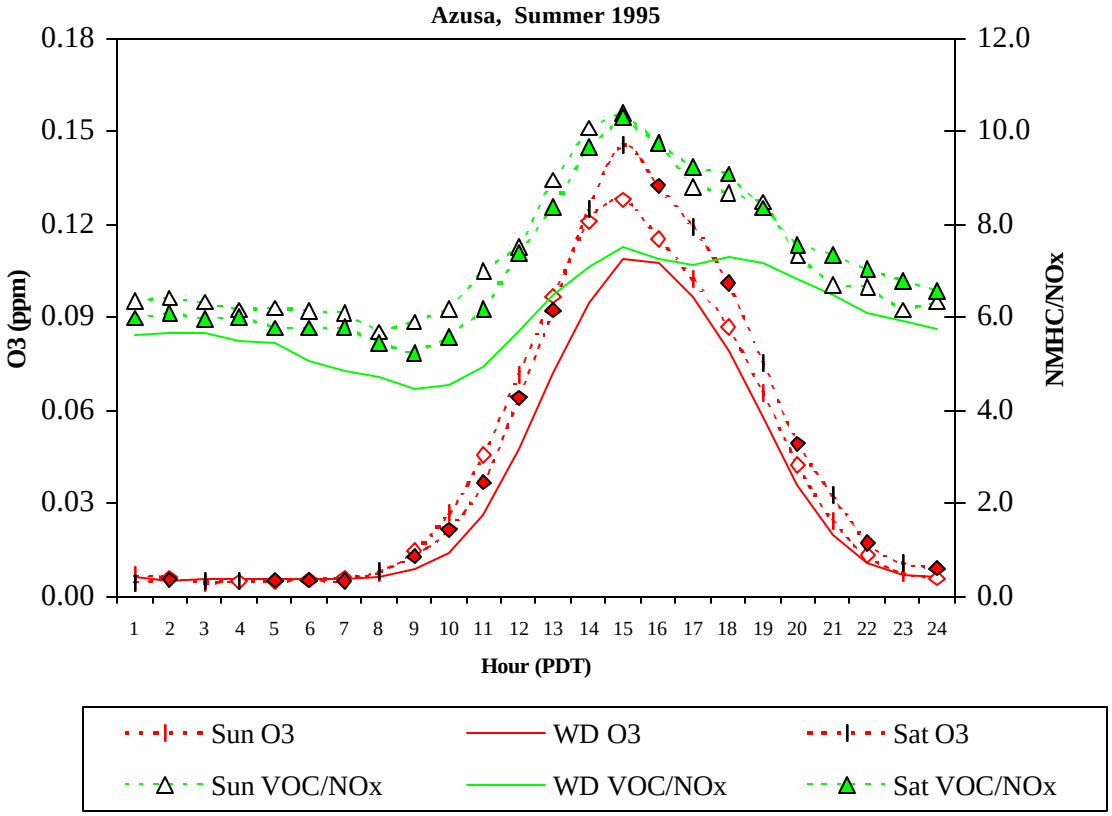



Figure 2. Average summer 1995 diurnal variations of $O_3$ and VOC/NOx at Azusa during weekday and weekend. Higher VOC/NOx on weekends result in higher rate of ozone formation.

The 7-8 a.m. NO, CO, and NMHC concentrations are substantially lower on weekends. Average 7-8 a.m. NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent of the average weekday concentrations, respectively. Average 7-8 a.m. CO and NMHC (estimated from CO) on Saturday and Sunday are 67-83 percent and 50-65 percent of the average weekday concentrations, respectively. NO emissions during this period inhibit radical formation by titrating ozone with NO. The end of the inhibition period occurs an hour earlier on weekends. Thus ozone formation begins earlier on weekends. On average, the ozone inhibition period ends about 0.5 to 0.7 hours earlier on Saturdays and about 1.1 to 1.3 hours earlier on Sundays. In general, ozone inhibition ends earlier in downwind areas and later in areas of highest density of fresh NO emissions. The concentrations of NO at 7-8 a.m. are about 3 to 4 times higher than before the morning commute period on weekdays. In contrast, NO is only slightly higher during 7-8 a.m. on Saturdays and is essentially constant between 4 to 8 a.m. on Sundays. While NO concentrations vary from site to site, the relative changes are similar at all sites. This general

pattern has changed very little in 18 years indicating that the degree of ozone inhibition by NO titration of ozone has remained fairly constant over this time period. Thus the magnitude and spatial extent of the weekend effect would not have changed if the delay in ozone accumulation by titration with NO were the only cause of the weekend effect.

The rate of and duration of ozone accumulation appear to be more significant parameters with respect to the weekend effect. Table 1 shows the average duration and rate of ozone accumulation during 1981 to 1999 for Sunday versus Wednesday. Compared to Wednesdays, the duration of ozone accumulation is about 1.2 hours longer on Sundays with no significant long-term changes. Duration of ozone accumulation is generally shorter in the western part of the basin and longer in the eastern basin. During 1981-84, the ozone accumulation rate was highest in the central basin and higher on weekdays than weekends at all sites. By 1995-98, the rate was highest in the eastern basin and higher on weekends than weekdays in most of the basin except the extreme western and eastern portions of the basin. On average, ozone accumulation rates were cut in half during the 18-year period with the largest reductions in the central basin. Table 1 and Figure 3 show that ozone accumulation rates were consistently lower on weekends than weekdays through most of the 1980's but became consistently higher on weekends during the 1990s. The switch from lower to higher ozone accumulation rates on weekends relative to weekdays coincides with an increase in the magnitude and spatial extent of the weekend effect in the SoCAB and with the steeper decline in the ozone during the 1990s, especially in the western and central parts of the Basin (see Figure 4).

Table 1
Trends in Duration and Rate of Ozone Accumulation in the SoCAB on Sunday, Wednesday, and Sunday Minus Wednesday, 1981-1999

| | **Duration of Ozone Accumulation (hours) [1]** | | | **Ozone Accumulation Rate (ppb/hour) [1]** | | |
|---|---|---|---|---|---|---|
| Years | Sun | Wed | Sun-Wed | Sun | Wed | Sun-Wed |
| 1981-84 | 5.5 ± 0.2 | 4.2 ± 0.3 | 1.3 ± 0.2 | 21.3 ± 1.0 | 24.3 ± 1.2 | -3.1 ± 0.8 |
| 1984-89 | 5.3 ± 0.3 | 4.2 ± 0.3 | 1.1 ± 0.1 | 19.5 ± 1.2 | 20.6 ± 1.6 | -1.1 ± 0.8 |
| 1990-94 | 5.2 ± 0.3 | 4.4 ± 0.3 | 0.8 ± 0.1 | 18.2 ± 0.9 | 16.3 ± 1.0 | 1.9 ± 0.6 |
| 1995-98 | 5.8 ± 0.3 | 4.5 ± 0.2 | 1.3 ± 0.2 | 13.8 ± 0.9 | 12.2 ± 0.9 | 1.6 ± 0.5 |

1 Twelve-site means and standard errors of the means.

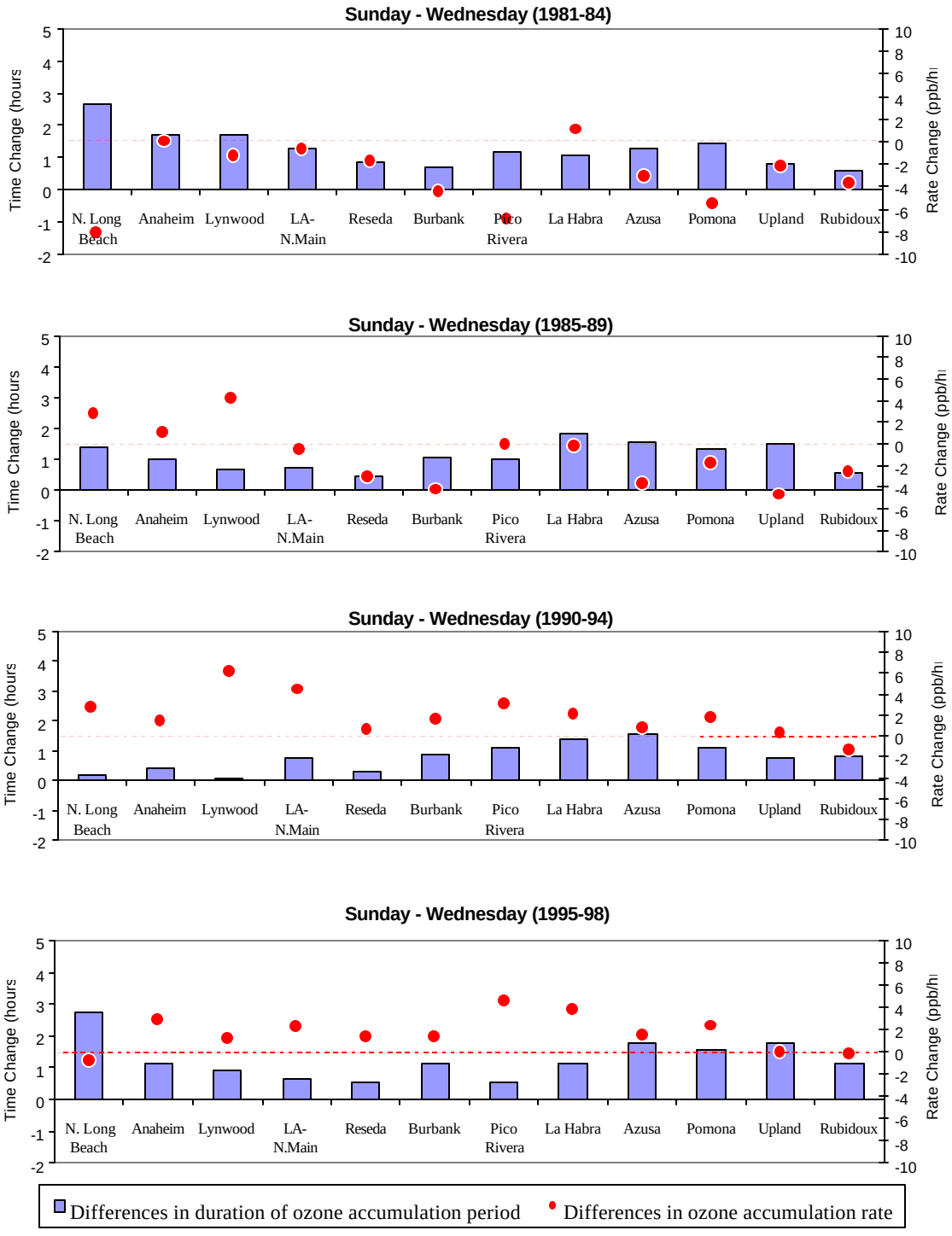



Figure 3. Sunday versus Wednesday differences in duration and rate of ozone accumulation for twelve sites in the SoCAB during 1981-84, 1985-89, 1990-94, and 1995-98. Sites are arranged in order of location from west to east with the western sites toward the left side of the plot.

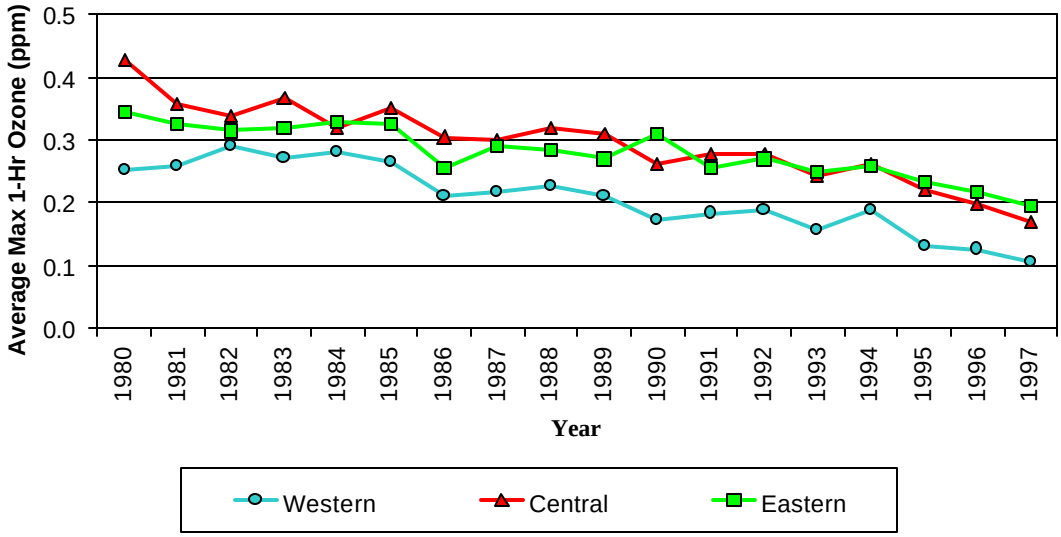



Figure 4. Trends in average maximum 1-hour ozone from 1980 to 1997 in the western, central and eastern portions of the South Coast Air Basin. Monitoring sites included in the averages are Los Angeles–N. Main, Lynwood, N. Long Beach, Anaheim, and La Habra, for Western, Azusa, Glendora, Pomona, and Upland for Central, and Riverside and Lake Gregory for Eastern.

Figure 5 shows the trends in the differences between Sunday and Wednesday ozone accumulation rates as three-year running averages for western, central, and eastern SoCAB sites. Changes in emission patterns from weekday to weekend in the 1980s resulted in little change in the ozone accumulation rate at western sites and generally lower weekend rates at central and eastern sites. The lower weekend ozone accumulation rate counteracts the shorter ozone inhibition period on weekends at central and eastern locations resulting in either no change or slightly lower ozone concentrations on weekends (i.e., no weekend effect). In the 1990s, the ozone accumulation rates were generally higher on Sunday than Wednesday. Coupled with the shorter inhibition period, ozone concentrations were consistently higher on weekends during the 1990s.

As explained in Section 4, VOC/NOx ratios[1] affect both the rate and efficiency of ozone production. The data show that differences between weekday and weekend VOC/NOx ratios have steadily increased over time. The ratios of the average 6-9 a.m. (PDT) VOC/NOx ratio on Saturday to that on Wednesday are 1.05, 1.06, 1.17, and 1.18 for the years 1981-84, 1985-89, 1990-94, and 1995-98, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17,

[1] As explained in Volume II, Section 2.2, NMHC is estimated from CO using an empirical relationship between NMHC and CO for data collected in 1995 and 1996. While these estimates are reasonably valid for determining day-of-the-week variations in NMHC concentrations and NMHC/NOx ratios for any year within the 18-year period of interest, they are probably not valid for estimating long-term trends in NMHC and NMHC/NOx ratios because the slope of the regression between CO and NMHC may have changed over time with changing emission control technology.

1.27 and 1.42. Similar differences are observed for the VOC/NOx ratios during the time of maximum ozone. The average weekday 6-9 a.m. (PDT) VOC/NOx ratios during the 1990s are about 7 compared to 8-9 on Saturdays and 9-10 on Sundays, and the ratios at maximum ozone are 10-11 on weekdays, 12-13 on Saturdays and 13-14 on Sundays. The morning VOC/NOx ratios are above the ridgeline in the ozone isopleth plot or VOC limited during weekdays and move toward the ridgeline on weekends. While greater carryover of VOC on weekends contributes to greater weekend morning VOC/NOx ratios, most of the increase is due to lower NO emissions during weekend mornings.

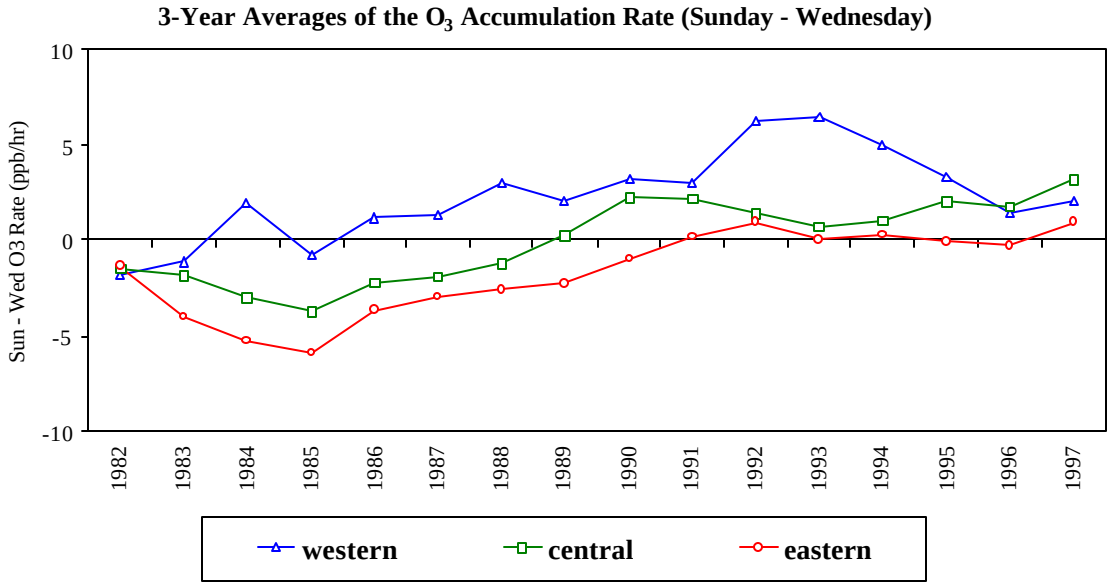



Figure 5. Sunday minus Wednesday differences in the duration and rates of ozone accumulation for the years 1981-84, 1985-1989, 1990-1994, and 1995-1998.

## 3.2 Summary of Available Emissions Data

Everyday observations and common sense suggest that aggregate variations in human activities, which follow a weekend-weekday pattern, are the most likely cause of the observed differences in weekend-weekday air quality. These human behavioral patterns directly govern weekend-weekday patterns of anthropogenic pollutant emissions. This section presents the findings of Phase I, Task 1: Review of Available Emissions Data. The objectives of Phase I, Task 1 were twofold: 1) develop a comprehensive list of emissions-related hypotheses and prioritize the list for further study and 2) identify existing sources of emissions data and assess the feasibility of gathering adequate data to refute or support each hypothesis. In order to formulate and prioritize a list of hypotheses, literature reviews were conducted, discussions with various government agencies were held, and potential sources of data were identified. Further study efforts were prioritized by examining each hypothesis, assessing the potential impact of each hypothesis on air quality, and determining the availability of existing data or the feasibility of collecting data to refute or support each hypothesis.

The SoCAB covers an area of approximately 6,500 square miles and has a population of more than 14 million. The California Air Resources Board (CARB) and the South Coast Air Quality Management District (SCAQMD) routinely publish emission inventories for the SoCAB. Daily average 1996 emissions of important ozone precursors, reactive organic compounds (ROG), NOx, and carbon monoxide (CO) are shown in Table 2-1 (California Air Resources Board, 1998). Table 2-1 lists total emissions by pollutant, broken down by major source categories (stationary, area, on-road mobile, and other mobile), and subcategories (e.g., gasoline vehicles). The emissions in Table 2-1 show that the on-road mobile source category is the single largest source category for ozone precursor pollutants, accounting for about 45, 64, and 69 percent of average daily ROG, NOx, and CO, respectively. Most of the on-road emissions are due to gasoline vehicles, but diesel vehicles contribute substantially to NOx emissions. Second to on-road mobile sources, stationary and area-wide sources are significant sources of ROG, while other mobile sources are currently a less important source of ROG. In contrast, other mobile sources generate relatively large emissions of NOx, while stationary and area-wide sources are less important NOx contributors. The vast majority of CO emissions are associated with on-road and other mobile sources. While CO emissions are not a major contributor to ozone formation they may serve as a tracer for mobile source emissions since they are primarily associated with mobile source fuel combustion.

Because the weekend effect appears to be partly a function of spatial and temporal characteristics of ozone precursor emissions, it is important to examine emissions in the SoCAB in the context of their spatial and temporal characteristics. In order to assess emissions on a day-of-week basis, emissions activity data must be obtained for both weekdays and weekends. Because ozone formation is dependent on precursor emissions emitted during the early part of the day, emissions activities occurring in the morning should be considered. Also, the diurnal differences in emissions activities between weekdays and weekends should be examined. For example, traffic patterns are likely to vary by both day-of-week and time-of-day. Because the extent of the weekend effect varies in different regions of the SoCAB, it is of interest to assess emissions activities on both a basin-wide level and a site-specific level.

Table 2. 1996 average daily emissions in the SoCAB (California Air Resources Board, 1998).

| Emissions Source | ROG (tons/day) | $NO_x$ (tons/day) | CO (tons/day) |
|---|---|---|---|
| Total – All Sources | 1,100 | 1,100 | 6,100 |
| Stationary Sources | 300 | 130 | 60 |
| Area-wide Sources | 210 | 34 | 430 |
| On-Road Mobile Sources | 500 | 700 | 4,200 |
| Gasoline Vehicles | 478 | 503 | 4,077 |
| Diesel Vehicles | 22 | 197 | 123 |
| Other Mobile Sources | 99 | 250 | 1,200 |
| Industrial Vehicles | 39 | 160 | 870 |
| Recreational Vehicles | 38 | 4 | 223 |
| Non-road (Trains & planes etc.) | 22 | 86 | 107 |

Identification of Existing Data

In order to identify existing sources of emissions activity data, literature reviews were conducted and discussions with several government agencies and industry experts were held. STI staff met with CARB staff to discuss existing data sources for all emissions source categories. At this meeting emissions activity data were identified for several important source categories. In addition to meeting with CARB staff, similar phone discussions with staff at the California Department of Transportation (Caltrans), the U.S. Census Bureau, the U.S. Marine Exchange, the U.S. Department of Energy, and the U.S. Department of Transportation Bureau of Transportation Statistics (DOT-BTS) were held. Literature reviews were conducted to identify recent studies regarding emissions activity patterns for all sources including the service industry, the manufacturing sector, and consumer products.

Since on-road mobile sources are the single largest source they received special attention in our review. There are many measures of on-road travel activity and several ways to compare them between weekdays and weekends. A few examples are listed below.

- Vehicle miles traveled (VMT)
- Fleet mix (trucks vs. cars)
- Cold/warm engine starts
- Trips (frequency, length, and geographic pattern)
- Trip chaining
- Cars [sports utility vehicles (SUVs) versus commuter cars]

- Diurnal patterns

The traditional view of weekend vs. weekday travel activity patterns, as reported in the Highway Capacity Manual, is that urban freeway traffic builds gradually from Monday through Friday, drops off on Saturday, and drops even further on Sunday. Rural and recreational routes have minimum traffic volumes mid-week, with pronounced peaks on Friday and Sunday. This result has been repeated for numerous urban centers, especially for Los Angeles. In a 1993-1995 study of Los Angeles vehicles equipped with data loggers, Magbuhat and Long (1996) showed that the frequency of cold starts follows the same general pattern as the urban traffic volumes. Additionally, several EPA reports document weekend-weekday activity information. Two recent EPA publications (Glover and Brzezinski, 1998a,b) illustrate that most weekend travel tends to begin at a later hour of day than weekday travel and that it continues to be relatively uniform throughout the day. Recently, SCAQMD staff have estimated weekend truck traffic counts to be approximately 40 percent of the truck traffic observed during an average weekday (Hsiao, 1999). The opposite phenomenon is observed for recreational boating patterns in California.

Because of the potentially large uncertainties in published emission inventories, one cannot reliably use published estimates of differences in weekday and weekend emissions. Thus, in this study, independent and verifiable differences in emissions must be identified. Detailed analyses of the differences between predicted emissions and observed hydrocarbon data show that the standard speciated emission inventories are not representative of ambient air quality data. This discrepancy can in part be attributed to outdated or unrepresentative profiles used to speciate total hydrocarbon emissions into individual chemical compounds measured in the ambient air. Particularly noteworthy is the lack of speciation profiles for recently introduced reformulated gasoline and reformulated solvents, inks, and surface coatings. The use of unrepresentative speciation profiles complicates the identification of differences between weekday and weekend day emissions from source types contributing significant hydrocarbon emissions. In Phase III, we plan to use the most recent source speciation profiles available to improve the success of this study.

Specific emissions changes on weekends may include the following:

- Increased refueling of gasoline-fueled vehicles (including Friday)
- Decreased number of trips of gasoline-fueled vehicles
- Increased home-related activity (e.g., lawn and garden equipment, surface coatings, paints, backyard barbecues, etc.)
- Decreased commercial-related activity (e.g., lawn and garden equipment, surface coatings, paints, etc.)
- Increased recreational activities (boating and other off-road mobile sources)
- Decreased industrial activity
- Decreased diesel (truck, bus, and train) activity

- Decreased commuter activity (shifts time and location of on-road mobile source emissions)
- Increased use of utility vehicles for personal use
- Decreased trip chaining

Because each of the activities listed emits different hydrocarbons, it should be possible to trace these types of changes with ambient data as well as estimate the changes through information gathered using limited surveys and traffic counts. During Phase II of this study, we will compile data that can be used to assess possible weekend effects. We will compile data for the year 2000 as well as historical data for 1997. Our priorities in compiling emissions-related activity data are collecting (1) monitoring site-specific data, (2) SoCAB-specific data, (3) California-specific data, and (4) typical data from locations throughout the country where available.

### 3.3 Review of Source Apportionment Analyses

Prior receptor modeling analysis performed by Desert Research Institute for the South Coast Air Basin (Fujita et al. 1997) was reexamined with respect to the day-of-the-week variations in source contributions. The analysis includes 252 canister samples that were collected by Desert Research Institute during the summer of 1995 (Zielinska et al., 1999). DRI collected samples for speciated hydrocarbons and carbonyl compounds twice a day (7-10 a.m. and 2-5 p.m. PDT) at downtown Los Angeles, Burbank and Azusa for six seven-day periods (July 8-14 and 17-23, August 1-7, August 31 - September 6, September 9-15 and 24-30) (252 samples). Source contributions are estimated for gasoline exhaust, diesel exhaust, gasoline evaporative loss (both motor vehicle and refueling), excess ethane and propane, composite surface coatings, and unidentified.

The average day-of-the-week variations in source contribution estimates ($ug/m^3$) show substantial reductions in the contribution of light-duty exhaust during weekend mornings. The weekend effect is particularly noticeable at downtown Los Angeles where the average light-duty exhaust contributions on Sunday mornings are half of the corresponding contributions on an average weekday morning. In comparison, the average light duty exhaust contributions on Sunday afternoons are about 80 percent of the corresponding contributions on an average weekday afternoon. For the three-site average, the contributions of gasoline vehicle exhaust on Sunday range from 70 to 80 percent of the average weekday contribution with the lowest ratios on Sunday mornings.

The corresponding ratios for diesel exhaust are considerably more variable than gasoline vehicle exhaust. The lowest weekend to weekday ratio for diesel occurs on Sunday afternoon (0.55). Although diesel exhaust has a relatively small effect on the weekday–weekend differences in NMHC, it has a much larger effect on weekday–weekend differences in NOx emissions because the ratio of NOx to NHMC emissions of diesel vehicles is substantially higher than that of gasoline vehicles. Gasoline evaporative emissions, ethane and propane, and unidentified NMHC have no significant day-of-the-week variation. Coating emissions on the

weekends are much lower compared to weekdays on a fractional basis. However, their absolute contributions are relatively low from the CMB analysis.

The results of the CMB analysis are based upon a limited number of samples. However, the results are consistent with the day-of-the-week variations for CO concentrations in the basin. Results indicate that diesel vehicles may be significant contributors to the large weekday-weekend changes in NO concentrations. While gasoline vehicle emissions are much lower on Sunday during the morning hours, the CMB results indicate that diesel vehicle emissions are lower during the afternoon as well. Lower NO emissions from diesel vehicles during these periods will contribute to higher VOC/NOx ratios during Sunday afternoons.

### 3.4 Analysis of SCOS97-NARSTO Meteorological and 3-D Ozone Data

The SoCAB has complex meteorology and air quality processes that result in large day-to-day variations in ozone concentrations. A large portion of the variations in ozone concentrations is attributable to day-to-day variations in meteorology and not to the day-to-day (or weekday to weekend) variations in emissions. Therefore, in the absence of a large data set of weekend and weekday ozone episodes, one must account for the effects of meteorology in analyses that compare weekend and weekday episodes.

Of the different parameters that represent meteorology, two that have a strong day-to-day influence on ozone concentrations are winds and mixing heights. Besides meteorology and emissions, aloft ozone also has some influence on surface ozone concentrations. A summary of our findings on winds, mixing heights, and aloft ozone is presented below.

Representativeness of mixing heights

Currently only two permanent radar profilers are operated in the SoCAB (e.g., LAX and ONT). We evaluated the usefulness of these data to represent mixing heights in the central portion of the SoCAB by comparing data from the existing sites with data from temporary profiler sites set up for SCOS97. We performed a variety of data analyses using products from radar wind profiler (RWP) and radio acoustic sounding system (RASS) data collected at 16 sites that operated throughout Southern California during the SCOS97 field study (MacDonald et al., 2000 a,b). In summary, we found that the existing sites of LAX and ONT do not represent the temporal and spatial variations in mixing heights over the entire basin well. In particular, the peak daytime mixing height, mixing growth rate, mid-morning average mixing height, time of peak mixing, and early morning mixing height in the central (El Monte) and the far eastern basin (Riverside) were not accurately represented by either LAX or ONT data.

Representativeness of winds

MacDonald et al. (2000a) used wind data collected by the 16 RWPs during three high-ozone episodes in 1997 (August 3-7, September 3-6, and September 26-29) to develop three-dimensional CALMET diagnostic wind fields. Using these wind fields, with the observed wind profiles at the 16 sites, we subjectively evaluated the regional representativeness of the temporal

and spatial variations in wind that can be obtained from profiler data collected at LAX and ONT alone. In summary, we found that the aloft winds measured at LAX are reasonably representative of winds at other surrounding coastal sites, but are often not representative of winds at mid- or east-basin sites. Also, we found that the winds measured at ONT are reasonably representative of winds at other surrounding inland sites, but are often not representative of mid- basin or coastal sites.

Mixing heights, winds, and aloft ozone

Previous analyses of aloft ozone data from SCAQS have shown the presence of deep layers (about 500 m) of high ozone concentrations over a wide portion of the SoCAB (e.g., Roberts and Main, 1992). The aloft ozone can contribute to he surface ozone concentrations when mixed to the surface during the day. During SCOS97 a Lidar located at El Monte (EMT) collected aloft ozone data from 90 m agl to about 2500 m agl during IOPs. Aloft wind and mixing height data were also collected at EMT. Using these data we evaluated the variability of the characteristics of these aloft ozone layers during ozone episodes and investigated the influence of the mixing heights and wind pattern on ozone concentrations.

In summary, we found that the interaction among winds, mixing heights, and ozone concentrations is too complex to form any definitive conclusions (in this preliminary analysis) about their relationship and how their relationship might influence differences in ozone concentrations between weekdays and weekends. Also, we found that the morning aloft ozone concentrations at EMT for selected 1997 episodes were about half the aloft ozone concentrations observed during selected episodes from the 1987 SCAQS field study. Although only a few days were compared, the observation does suggest that contribution of aloft ozone to surface ozone may not be as significant now as it was in 1987.

# 4. PRELIMINARY CONCEPTUAL EXPLANATION OF THE "WEEKEND EFFECT"

The following discussion integrates the retrospective analysis of existing ambient, emissions inventory and mesoscale meteorological data in the SoCAB with the current understanding of ozone formation into a preliminary conceptual explanation of the weekend effect.

The WE effect is rooted in ozone's complex photochemistry in which the rate of $O_3$ production is a non-linear function of the mixture of VOC and NOx in the atmosphere. Depending upon the relative concentrations of VOC and NOx and the specific mix of VOC present, the rate of $O_3$ formation can be most sensitive to changes in VOC alone or to changes in NOx alone or to simultaneous changes in both VOC and NOx. Ozone is produced in the atmosphere by the reaction of a ground state oxygen atom, $O(^3P)$, and molecular oxygen ($O_2$). While $O_2$ is abundant in the atmosphere, free oxygen atoms are not. At lower altitudes, the photodissociation of nitrogen dioxide ($NO_2$) into nitric oxide (NO) and atomic oxygen (Reaction 1) is the only significant source of oxygen atom. The oxygen atoms react with $O_2$ to produce $O_3$ (Reaction 2). However, NO reacts rapidly with $O_3$ to regenerate $NO_2$ (Reaction 3). The first and third reactions occur rapidly, establishing a steady-state equilibrium ozone concentration $[O_3]$ that is determined by the following "NO-photostationary state equation,"

$$[O_3] = \frac{J_1[NO_2]}{k_3[NO]}$$

where $J_1$ is the photolysis frequency of Reaction (1), $k_3$ is the rate constant for Reaction (3), $[NO_2]$ is the concentration of nitrogen dioxide and [NO] is the concentration of nitric oxide. One $O_3$ molecule is required to regenerate $NO_2$ from NO, so these reactions are insufficient, by themselves, to create excessive ozone levels. When volatile organic compounds are present, however, their photochemical oxidation produces hydroperoxy radicals ($HO_2$) and organic peroxy radicals ($RO_2$), which react with NO to form $NO_2$ without destruction of ozone, thereby allowing ozone to accumulate by increasing the ratio of $[NO_2]$ to [NO].

The hydroxyl radical (HO) initiates the oxidation of VOCs that form the peroxy radicals. VOCs are consumed in the sequence of ozone formation, while HO, $HO_2$, and NOx act as catalysts. Termination occurs by reaction of HO with $NO_2$ to form nitric acid ($HNO_3$) or when $HO_2$ combines to form hydrogen peroxide ($H_2O_2$). The production efficiency of $O_3$ per molecule of NOx varies with total concentration of NOx and the ratio of VOC to NOx. At low VOC-to-$NO_2$ ratios, HO reacts predominantly with $NO_2$, removing radicals and retarding $O_3$ formation. Under these conditions, a decrease in NOx concentration favors $O_3$ formation. High ratios of VOC to NOx concentration favor HO reaction with VOCs that generate new radicals that accelerate $O_3$ production. At a sufficiently low concentration of NOx, or a sufficiently high VOC-to-$NO_2$ ratio, a further decrease in NOx favors peroxy radical-peroxy radical reactions, which retard $O_3$ formation by removing free radicals from the system. At a given level of VOC, there exists a NOx mixing ratio at which a maximum amount of ozone is produced. This

optimum VOC/NOx ratio depends upon the reactivity to HO of the particular mix of VOCs that are present. For ratios less than this optimum ratio, increasing NOx decreases ozone.

The ozone isopleth diagram shown in Figure 6 illustrates the dependence of $O_3$ production on the initial amounts of VOC and NOx. The ozone ridge in the isopleth diagrams corresponds to the maximum $O_3$ concentration that can be achieved at a given VOC level. The VOC/NOx ratio at the ridgeline is about 10 to 12. The HO radical chain length, which is the number of times a newly formed HO radical is regenerated through radical chain propagation before it is destroyed, reaches a maximum at this VOC/NOx ratio. Thus, the ridgeline corresponds to the VOC/NOx ratio at which $O_3$ is most efficiently formed. Above the ridgeline, a reduction in NOx lowers the rate at which HO and $NO_2$ are removed by formation of $HNO_3$ and leads to an increase in maximum $O_3$. This region is commonly described as "radical-limited" or "VOC-limited" (i.e., lowering VOC most effectively reduces $O_3$). "NOx-disbenefit" refers to a situation when NOx reduction leads to an increase in ozone. This disbenefit occurs only in the VOC-limited region. Below the ridgeline at low NOx concentrations there is a large region where lowering NOx most effectively reduces $O_3$ and large reductions in VOC have practically no effect on maximum $O_3$. This region is described as "NOx-limited."

VOC/NOx ratios vary within air basins, resulting in either NOx-limited or VOC-limited areas depending upon the time of day, the mix and timing of additional fresh emissions, and pattern of pollutant transport. Because HO reacts more rapidly with $NO_2$ than with VOCs, the instantaneous VOC/NOx ratios tend to increase with time. Thus NOx is removed more rapidly from the system than VOCs and accounts for the tendency for ozone formation to be NOx-limited in areas downwind of the urban center. Consequently, NOx disbenefit that may be associated with reduction in NOx emissions is generally limited to regions in and near urban centers, and NOx reductions should reduce $O_3$ in the surrounding region. However, addition of dispersed NOx sources in downwind suburban areas may extend the area of VOC limitation further downwind.

In addition to the rate of ozone formation, the intensity and spatial extent of the WE effect also depend upon the degree of inhibition of ozone accumulation due to titration of $O_3$ with NO. The photolysis of $O_3$ produces an excited oxygen atom, $O(^1D)$ and its subsequent reaction with water is the primary source of HO radical. NO exists in excess of $O_3$ in the urban center overnight, and suppresses the concentration of $O_3$ to zero or near zero in the surface layer. Fresh NO emissions during the morning commute prolongs the inhibition of ozone accumulation after sunrise. During this inhibition period, the photolysis of carbonyl compounds and smaller contributions of nitrous acid (HONO) and other radical precursors are the primary source of HO radicals until a sufficient amount of NO has been converted to $NO_2$. $O_3$ carried over aloft from the previous day can mix down in the morning and contribute $O_3$ and radicals to the developing surface ozone chemistry. Lower NOx emissions on weekends decrease NO titration of the $O_3$ newly formed at the surface and the ozone transported from aloft. Accordingly, ozone formation should begin earlier on weekends.

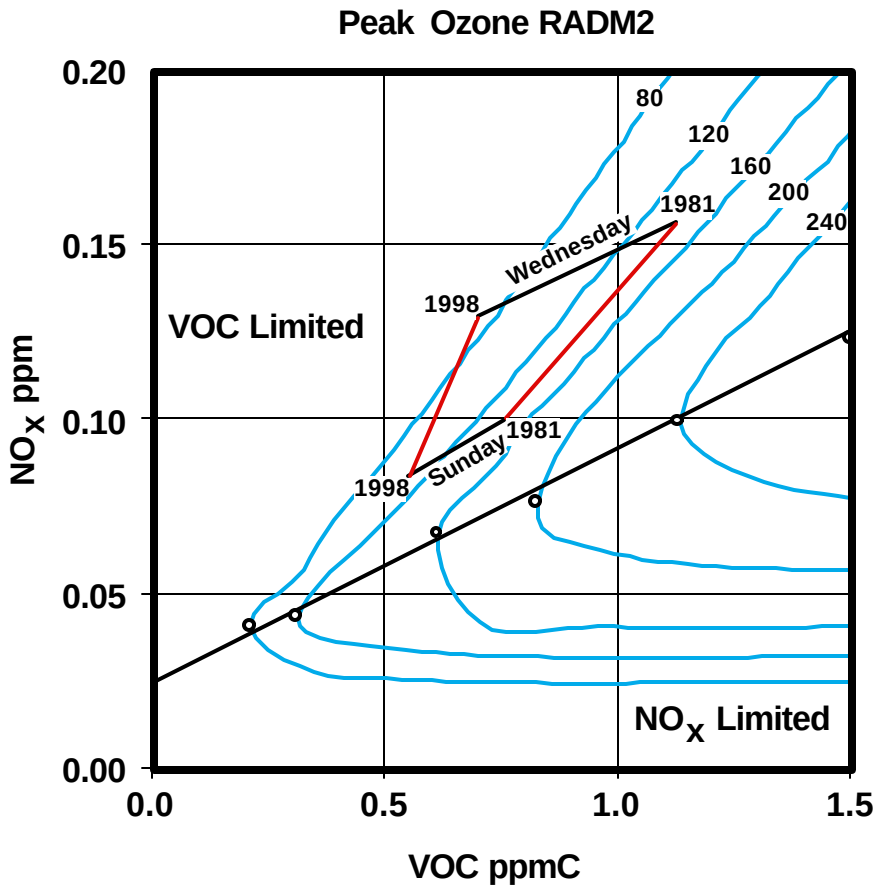



Figure 6. Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized as VOC- or NOx-limited. The isopleth plot was generated using the Ozone Isopleth Plotting Program, Research Version (OZIPR) with the RADM2 chemical mechanism (Stockwell et al. 1990). The trapezoid in the isopleth diagram illustrates how the relationship of $O_3$ with VOC and NOx may have evolved in the central portion of the Basin in order to produce the changes in the weekend effect observed from 1981 to 1999.

Analysis of the ambient data indicates that the intensity and spatial extent of the WE effect are correlated with weekday-weekend differences in the degree of ozone inhibition and rates of ozone accumulation. Lower NO concentrations and higher $NO_2$/NOx ratios during weekend mornings decrease the removal of ozone by titration with NO, thereby allowing ozone to accumulate about an hour earlier on weekends compared to weekdays. The amount of delay in ozone accumulation due to greater NO titration of ozone on weekdays is similar throughout the Basin and has remained relatively constant from 1981 to 1999. In contrast, the rate of ozone accumulation from the end of ozone inhibition to the time of ozone maximum decreased by one-half over the same time period with the largest reductions occurring in the central basin. Rates of ozone accumulation were consistently lower on weekends than weekdays through most of the 1980s but became consistently higher on weekends during the 1990s. Central and eastern parts of

the Basin showed either no change or slightly lower ozone concentrations on weekends (i.e., no weekend effect) in the 1980s because the shorter ozone inhibition periods were offset by the lower rates of ozone accumulation. A switch to higher weekend ozone accumulation rates in the 1990s, coupled with a shorter inhibition period, resulted in higher weekend ozone concentrations during the 1990s and a strengthening of the WE effect in the Basin.

The trapezoid in the ozone isopleth diagram in Figure 6 illustrates how the relationship of $O_3$ with VOC and NOx may have evolved in the central portion of the Basin in order to produce the observed changes in the weekend effect from 1981 to 1999. The sides of the trapezoid are based upon the following findings from our analysis of the ambient data.

1. Little or no WE effect in the 1980s shows that changes in emissions between weekends and weekdays were such that maximum ozone concentrations remained on roughly the same $O_3$ isopleth contour line between weekday and weekend (right line).

2. A more pronounced WE effect in the 1990s shows that changes in emissions between weekends and weekdays were such that maximum ozone concentrations shift from a lower to a higher $O_3$ contour between weekday and weekend (left line).

3. Changes in VOC/NOx ratios between weekday and weekend increase from 1981 to 1998, especially in 1990s, toward higher weekend VOC/NOx ratios. The ratios of the average 6-9 a.m. (PDT) VOC/NOx ratio on Sunday to that on Wednesday are 1.10 and 1.42 for the years 1981-84 and 1995-98, respectively (slope of bottom line greater than slope of top line).

4. Reductions in ozone concentrations from 1981 to 1998 are greater on weekdays than weekends. Ozone concentrations in 1995-98 expressed as ratios of the 1981-84 values range from 0.54 to 0.59 on Monday through Friday and 0.70 on Sunday (top line longer than bottom line).

The air quality data analysis shows that the WE effect is associated with day-of-week differences in the degree of ozone inhibition and ozone accumulation rates. The early morning formation of ozone is initiated by photolysis of HONO, HCHO, and PAN or photolysis of $O_3$ entrained from aloft. But the concentration of NO and the $NO_2$/NOx ratio are the key parameters with respect to the length of the ozone inhibition period. VOC/NOx and photochemical reactivity of the VOC mixture determine the rate of ozone formation. Day-of-the-week differences in these air quality parameters arise from day-of-the-week changes in the spatial and temporal distribution of VOC and NOx emissions due to changes in activity patterns. The association between the spatial and temporal patterns and magnitude of NOx and VOC emissions and air quality parameters are determined by the diurnal and day-to-day variations in synoptic and mesoscale meteorology, which lead to varying spatial extent and intensity of the WE effect.

Meteorology is the dominant factor controlling the change in ozone air quality from one day to the next. Synoptic and mesoscale meteorological features govern the transport of emissions between sources and receptors, affecting the dilution and dispersion of pollutants during transport and the time available during which pollutants can react with one another to form ozone. During summer, the sea-land breeze is strong during the day with a weak land-sea

breeze at night. Owing to the high summer temperatures and extensive urbanization in the SoCAB, the land surface temperature does not usually fall below the water temperature at night, and nocturnal and morning winds are less vigorous than daytime winds. The land surface cools sufficiently to create surface inversions with depths as shallow as ~50 m. Surface heating usually erodes the surface and marine layers within a few hours after sunrise each day. Summertime flow patterns are from the west and south during the morning, switching to predominantly westerly winds by the afternoon. The land/sea breeze circulation moves air back and forth between the SoCAB and the Pacific Ocean, as well as along the coast to other air basins. Although vertical mixing and horizontal advection can have a large impact on local ozone concentrations, day-of-the-week variations in meteorological conditions tend to average out on the time scale of several years.

The weekend effect is greatest where the ozone formation is more VOC-limited during the weekday and less VOC-limited during the weekends, and ventilation occurs before the potential maximum ozone level is produced. Assuming that there are sufficient VOC and NOx, the amount of $O_3$ formed is proportional to the duration of $O_3$ accumulation period. Greater rates of $O_3$ formation lead to more ozone and the rate of ozone formation increases with increasing VOC/NOx ratios. Under typical summer transport pattern in the Basin, less time is available near the coast for ozone to accumulate before ventilation occurs. The ozone accumulation period is about 3 hours near the coast and increases to about 6 hours in the eastern part of the Basin. The ozone accumulation period is about an hour longer on weekends because ozone formation begins an hour earlier on weekends. These facts have several important consequences for the WE effect. Near the coastline, the day-of-the-week differences in the VOC/NOx ratios have a more dominant effect on WD versus WE peak ozone concentrations due to the short time for ozone accumulation. In the eastern Basin, day-of-the-week differences in the initial VOC/NOx ratios and the resulting differences in $O_3$ formation rates have less effect on WD versus WE peak ozone concentrations because of the longer $O_3$ accumulation time that allows ozone formation to proceed closer to completion. During transport to the east side of the Basin, VOC/NOx ratios increase due to more rapid removal of NOx versus VOC resulting in increased rates of ozone formation. Thus we would expect that the WE effect will reach the maximum intensity somewhere in the central Basin due to the competing factors of $O_3$ accumulation time and rate of $O_3$ formation.

# 5. PHASE II PLAN

The Phase I air quality data analysis and results of other investigations lead to several alternative hypotheses for the WE effect. This section describes these hypotheses and the data analysis approach and measurement plan for Phase II to address these hypotheses. Because of resource limitations and time constraints, the proposed experimental design focuses on short-term investigations of emissions-related hypotheses. The investigation of meteorological influences of the WE effect requires much longer term investigations than allowed by the current scope of Phase II. These factors will be addressed in Phase III utilizing supplemental data sources, which include historic SCAQMD monitoring data, recent PAMS hydrocarbon data, and relevant data from recent field studies such as the 1997 Southern California Ozone Study (SCOS-NARSTO) and the Central California Ozone Study (CCOS).

## 5.1 Hypotheses for WE Effect

The hypotheses for the day-of-week differences in ozone consist of a set of hypothetical effects related to air quality, photochemistry, meteorology, and emissions. One subset of hypotheses is related to the interactions of ambient concentrations of VOC and NOx, chemical transformations, and transport that affect the day-of-the-week differences in the diurnal evolution of ozone chemistry. The second subset hypothesizes emission-activity differences between weekdays and weekends that affect the photochemistry so that changes in emissions could explain day-of-the-week differences in observed ambient concentrations of NOx, VOC, and VOC/NOx ratios.

There are seven hypotheses related to air quality that are categorized into three types. The first type is related to changes in $O_3$ inhibition, the second type is related to ozone formation rates, and the third type is related to day-of-the-week differences in photolysis rates. Under each of the seven air quality hypotheses, emission hypotheses that are the presumed cause of the air quality effect are identified (by small letters).

**A. Changes in $O_3$ inhibition on weekends.**

1. Lower NO concentrations on weekend mornings result in less ozone inhibition than on weekday mornings.

    a. Heavy-duty diesel truck (and bus, train) activity is less on weekends during the ozone inhibition period than on weekdays resulting in lower NO concentrations and less ozone inhibition.

    b. On-road light-duty gasoline vehicular activity is less on weekends during the ozone inhibition period than on weekdays resulting in lower NO concentrations and less ozone inhibition.

**B. Changes in ozone formation rates due to changes in VOC/NOx ratio or other factors.**

2. Lower NO concentrations on weekend mornings result in higher VOC/NOx ratios than on weekday mornings.

   a. Heavy-duty diesel truck (and bus, train) activity is less on weekends during the ozone accumulation period than on weekdays resulting in higher VOC/NOx ratios and higher ozone formation rates.

   b. On-road light-duty gasoline vehicular activity on weekends is similar or higher than weekdays during the ozone accumulation period. Lower diesel NOx emissions during the same period results in higher weekend VOC/NOx ratios during this period.

3. Higher VOC concentrations on weekends result in higher VOC/NOx ratios than on weekday mornings.

   a. Use of off-road recreational vehicles, lawn and garden equipment, backyard barbecues, and household solvents are increased on weekends compared to weekdays resulting in higher weekend VOC/NOx ratios.

4. Greater carryover of VOC concentrations relative to NOx on Friday and Saturday evenings results in higher VOC/NOx ratios and increased rate of ozone formation on Saturday and Sunday mornings.

   a. Heavy-duty diesel activity is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carry over of pollutants with higher VOC/NOx ratios.

   b. Light-duty gasoline vehicle traffic is increased while heavy-duty diesel traffic is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carry over of pollutants with higher VOC/NOx ratios.

5. Greater contribution of aloft VOC to surface VOC concentrations on weekends during the ozone accumulation period increases the rate of ozone formation compared to weekdays.

6. Because $O_3$ inhibition is lower on weekends, HONO, HCHO, PAN, or other early-morning radical sources increase in relative importance. These radical sources may be contained in the surface or aloft carryover.

**C. Higher photolysis rates on weekends**

7. Lower PM concentrations during weekends increases the direct and scattered UV available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

a. Lower vehicle traffic on weekends, especially heavy-duty diesel truck (and bus, train), results in lower direct emissions of soot particles that absorb light.

b. Lower vehicle traffic on weekends, especially heavy-duty diesel truck (and bus, train), results in lower emissions of NOx that reacts to form secondary nitrate particles.

## 5.2 Data Analysis Approach

The proposed experimental design for the Phase II field study focuses on short-term investigations of emissions-related hypotheses. DRI will conduct more detailed time-resolved measurements to test the hypothesized relationship between emissions sources and the diurnal and day-of-the-week variations in CO, NO, NOx, VOC, VOC/NOx and $NO_2$/NOx. The field study measurements focus on attribution of ambient precursor concentrations to major sources of VOC and NOx. STI will gather and compile existing and new emissions data that will support testing of weekend/weekday emissions hypotheses as described above.

Daily local meteorology will not affect our emission measurements. It is expected that the Phase II measurements will capture the day-of-the-week differences in traffic characteristics and in the emissions of NOx and VOC and the associated VOC/NOx ratios. We will examine the data to investigate the effect of surface and aloft carryover of VOC and NOx and their effect on surface VOC and NOx concentrations during the ozone inhibition and accumulation periods. It must be recognized that the latter effects are heavily influenced by the prevailing meteorology during the field study and may not be completely representative of the seasonal average.

During Phase III, we will make comparisons between weekend and weekday ambient air quality data collected from as far back as July 1997 through summer 2000. These analyses will be limited because the emissions activity data will not be day specific as in the field study. The combination of more statistically robust number of days in this analysis with the day-specific approach of the field study data analysis will provide substantial information to help improve our understanding of the WE effect.

The investigation of the possible changes in photolysis rates on WE effect will be performed by analyzing an existing data set of UV actinic flux collected near a freeway at Sunol, CA during the summer 2000 Central California Ozone Study (CCOS). The photolysis of nitrogen dioxide, ozone, formaldehyde and other carbonyl containing compounds are the initial steps in the production of photochemical air pollutants. The photolysis rate of an air pollutant is the product of the compound's mixing ratio and its photolytic rate parameter. The photolytic rate parameter is the integral over all wavelengths of the product of the compound's absorption cross-section, quantum yield and actinic flux. The actinic flux was measured with a diode array spectrometer that has a hemispheric sampling head ($2\pi$ response). The data record extends for a period of over two months. Therefore, it will be possible to make some reasonably valid weekend to weekday comparisons of the actinic flux according to wavelength and, hence, photolysis rates of key reactive species. Correlations of the actinic flux will be made with concurrent data for $O_3$, black carbon, and particulate nitrate.

The investigation of meteorological influences on the WE effect require much longer term investigations than allowed by the scope of Phase II. These factors will be addressed in Phase III utilizing other sources of data. These supplemental data source include historic SCAQMD monitoring data, recent PAMS hydrocarbon data, and relevant data from recent field studies such as the 1997 Southern California Ozone Study (SCOS-NARSTO) and CCOS.

### 5.3 Phase II Measurement Plan

The field measurements involve two approaches: supplemental measurements at existing SCAQMD monitoring sites and mobile sampling during periods that coincide with overnight carryover of $O_3$ precursors, $O_3$ inhibition, and $O_3$ accumulation. Supplemental measurements by DRI at the monitoring stations include hourly $C_2$ to $C_{11}$ volatile organic compounds by automated gas chromatography with ion-trap mass spectrometry at Azusa, continuous black carbon by light absorption with an aetholometer (approximately 5-minute averages) at Azusa and Pico Rivera, and 3-hour composite Tenax samples for $C_8$ to $C_{18}$ hydrocarbons beginning at 0200, 0600, and 0900 PDT on 9/30, 10/1, 10/2, 10/4, 10/6, 10/7, and 10/8. ARB will collect canister samples at Los Angeles – N. Main for speciated hydrocarbons on the same schedule, and SCAQMD will measure 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera. The analysis of the data in Phase III of the study will also take advantage of the CO and NOx measurements from the SCAQMD's monitoring network.

Primary pollutants (CO, NO, black carbon [BC] and speciated hydrocarbons) will be measured simultaneously in a mobile van along several freeway loops in different areas of the basin. Carbon monoxide (TEI 48), NO/NOy (TEI 42S) and black carbon estimated from light absorption (Anderson RTAA-1000 aethalometer) will be measured continuously with averaging times of 1, 1, and 5 minutes, respectively. Integrated canister and Tenax cartridge samples will be collected over a period of approximately 50 minutes during each freeway loop and at fixed locations. Sonoma Technology, Inc. will conduct concurrent traffic and emission source surveys during the field study.

Mobile sampling will be conducted during the carryover period between 2-5 a.m. (PDT), the ozone inhibition period between 6 to 9 a.m., and during the ozone accumulation period between 9 a.m. and noon. Measurements will be made on Saturday (9/30), Sunday (10/1), Monday (10/2), Wednesday (10/4), Friday (10/6), Saturday (10/7), and Sunday (10/8) along the following loops and fixed locations.

- 0200 to 0245 - Industry Hills Conference Center (overflow parking lot on the south end of the conference center) on all days.
- 0300 to 0345 - Covina Loop (east on S-60 from Azusa Avenue onramp, north on S-57, west on I-10 to I-5) on all days.
- 0415 to 0500 – Dodger Stadium (four loops around the perimeter of the Stadium) on all days.
- 0515 to 0600 – Compton Loop (south on S-110 from Stadium Way onramp, east on I-405, north on I-710 to I-10) on all days.

- 0630 to 0715 – Source-dominated samples for SI vehicle exhaust profile (fixed location sampling on southbound S-110 just south of Stadium Way onramp) on 10/2, 10/4, 10/6, 10/7 and 10/8. The Pasadena Freeway is restricted to automotive traffic only.

- 0730 to 0815 – Dodger Stadium on all days.

- 0830 to 0915 – Compton Loop on all days.

- 0930 to 1015 - Covina Loop (east on I-10 at I-710, south on S-57, west on S-60 to Azusa Avenue offramp) on all days.

- 1030 to 1115 - Industry Hills Conference Center on all days.

- 1130 to 1215 - Pomona Loop (east on S-60 at Azusa Blvd onramp, north on I-15, west on I-10, north on 210 to Azusa Avenue offramp on 10/2, 10/4, 10/6, 107, and 10/8.

Five sets of canister and Tenax samples and continuous CO, NO, NOy and black carbon measurements will also be taken at a truck stop near I-10 and I-15. Measurements will be made during the early morning hours from 0100 to 0500, and will consist of three sets of samples at the truck stop and upwind samples before and after the truck stop samples. Additionally, ten gasoline and two diesel fuel samples will be collected for analysis of speciated VOCs. The canister samples will be analyzed in the laboratory for CO, $CO_2$, methane, MTBE, and $C_2$-$C_{11}$ hydrocarbons, and $C_8$-$C_{18}$ hydrocarbons will be quantified from Tenax samples.

The mobile sampling data will be used to characterize the diurnal variations in relative contributions of gasoline and diesel vehicles to the ambient level of ozone precursors by day of the week. For each loop, the time series of NO and CO will be related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbons) and spark-ignition exhaust (MTBE) for the carryover, ozone inhibition, and ozone accumulation period by day of the week. From the NO, CO, BC, MTBE, and $nC_{10}$-$nC_{15}$, we will estimate the fraction contributions of spark-ignition and compression-ignition emissions of NO, and NMHC as described in Section 4 of Volume II of this report.

In addition to the relative contributions of on-road gasoline and diesel vehicles, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations will also allow for source attribution of other sources of VOC by time of day and day of the week. These analyses will address questions regarding the source contributions of VOC carried over from the previous evening and the relative importance of on-road versus other area sources in the diurnal variations in VOC/NOx ratios. Diurnal variations in VOC composition will be used to determine day-of-the-week differences in ozone formation potential and reactivity of the VOC mix.

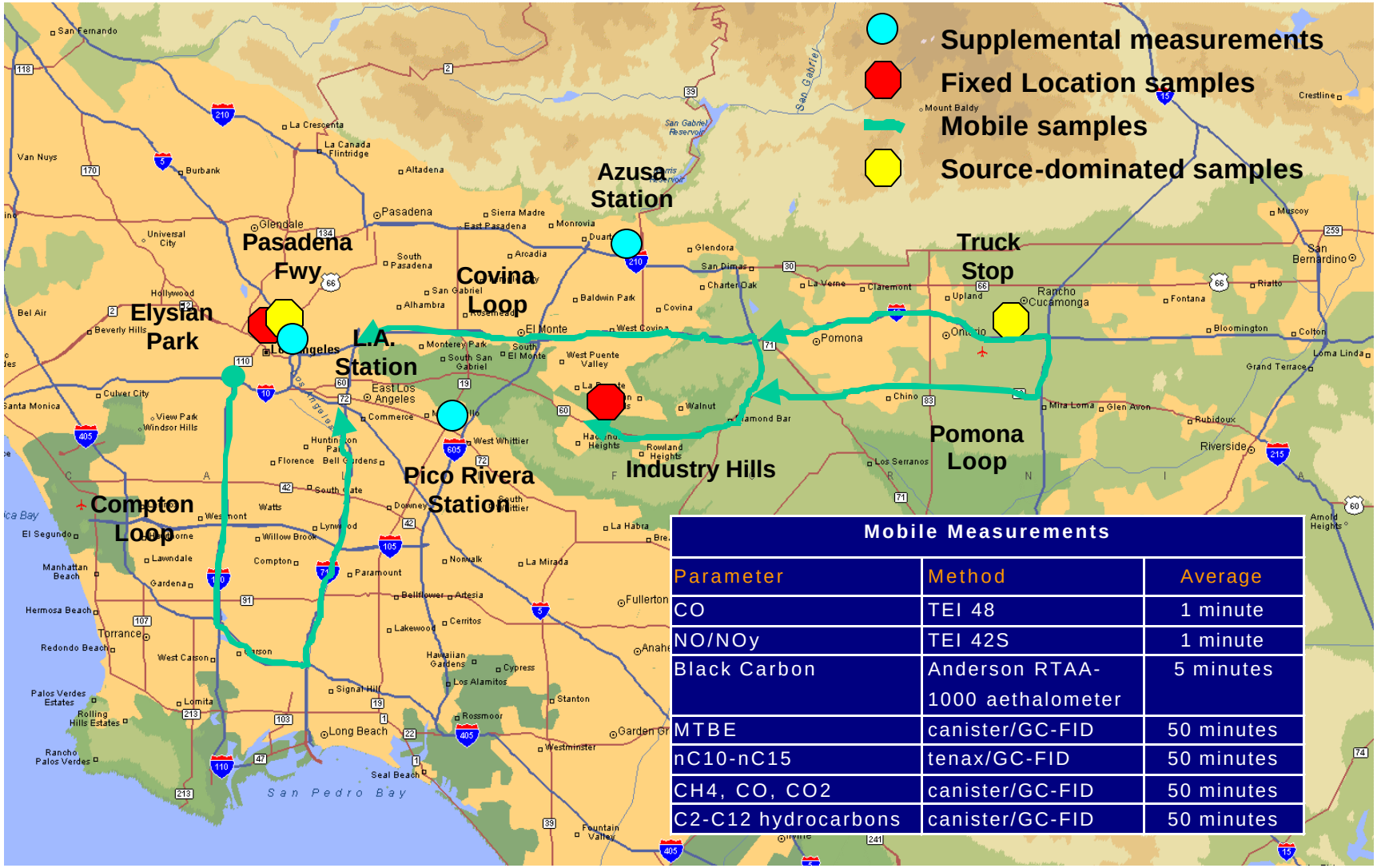



Figure 7. Sampling locations during the Phase II Field Study.

## 5.4 Emission Inventory Development

STI will gather and compile existing information and new data that will support testing of weekend/weekday emissions hypotheses as described above. Data to be gathered in Phase II of this project include regional data collected by others but compiled for analysis by STI such as:

- Caltrans weight in motion (WIM) data collected hourly, by day of week, and by vehicle type for numerous freeways in southern California
- Major point source activity data for the Los Angeles airport, power plants, oil refineries, etc.
- Surface street on-road mobile source vehicular activities data
- Area source activity data for lawn/garden equipment use, home maintenance, etc.
- Off-road mobile source activity data such as for recreational vehicles (e.g., marina and rural fuel sales), aircraft, and freight and commuter train operating schedules

In addition to regional data we will also be collecting site-specific information near the monitoring sites of LA North Main, Pico Rivera, and Azusa, and a site to be located near the Industrial Hills Sheraton Resort, including.

Verify ("ground truth") all emission sources within 2 km (i.e., roughly one hour of air parcel travel time) of each monitoring site.

- Visually survey weekday versus weekend activities during morning hours over multiple days (i.e., repeated visual surveillance). During the monitoring period, STI's subcontractor, Wiltech, will deploy automated traffic counters in each neighborhood of the four monitoring sites. Total traffic counts will be collected at two sites and collocated counts by vehicle class will be collected at one site in each neighborhood. In each neighborhood, a representative arterial/collector street and a representative local street will be selected for traffic counts. The traffic counters will be operated for ten days, starting on a Friday to capture two weekends and one workweek.
- Digital Orthophoto Quadrangle (DOQ) images will be obtained from the United States Geologic Survey (USGS) for a 2-km area surrounding each ambient monitoring site. The DOQ images combine the visual characteristics of a photograph with the geometric qualities of a map and can be used to identify detailed land features such as residential neighborhoods that are not present on generic maps. The DOQ images can be incorporated into a geographic information system (GIS), and, unlike a standard aerial photograph, relief displacement in the DOQ images can be removed so that ground features are displayed in their true ground position. As part of this task, we will also provide detailed geographic information system (GIS) maps showing each monitoring site and the surrounding area using existing available electronic databases (as is) e.g., the 1997 electronic yellow pages.

- Perform limited phone and mail surveys of actual emissions sources (small point and area sources) within about 2 km around each monitor. The form for residential surveys is shown below.

**DAILY ACTIVITY SURVEY for *FRIDAY SEPTEMBER 29, 2000***
*Please answer these questions about activities at your household on this day, and indicate when they occurred:*

| | | | *When? (check all that apply):* |
|---|---|---|---|
| Was a barbeque grill used? | ___yes | ___no | morning___ afternoon___ evening___ |
| Was a fireplace used? | ___yes | ___no | morning___ afternoon___ evening___ |
| Was gasoline or diesel poured from or into a gas can? | ___yes | ___no | morning___ afternoon___ evening___ |

How many times did a passenger vehicle depart from your household?

__0 __1 __2 __3 __4 __5 __more than 5 times morning___ afternoon___ evening___

*Please check each of the materials that were used at your household on this day, and indicate when they were used:*

___ paints, varnishes, stains, thinners, solvents, or degreasers morning___ afternoon___ evening___
___ consumer products such as hair sprays, dyes, nail polishes, polish removers morning___ afternoon___ evening___

☐ aerosol products
___ paving or roofing materials (tars, asphalts) morning___ afternoon___ evening___
___ motor oils, gear oils or fluids, or brake fluids morning___ afternoon___ evening___
___ gasoline-powered yard equipment (lawnmowers, weedwackers, blowers) morning___ afternoon___ evening___
___ pesticides or fertilizers morning___ afternoon___ evening___

Did you consider today a ___typical work day ___holiday/vacation day ___regular day off? (Please check one.)

On what date did you complete this card? (Please circle one.)

Fri 9/29/00 Sat 9/30/00 _____Sun 10/1 /00 _____Mon 10/2/00 Tue 10/3/00
Wed 10/4/00 Thu 10/5/00 Fri 10/6/00 _____Sat 10/7/00 _____Sun 10/8 /00

THANK YOU! Please drop this card in the mailbox—you don't need a stamp.

Figure 8. Residential survey form for small point and area sources

## 5.5 Meteorological And Aloft Air Quality Analysis Plan

STI will examine the meteorology on the selected weekend and weekday episode days during the summer/fall 2000 measurement period to determine if the meteorology was similar between days of the week. Because it is not likely that there are many days to compare with very similar meteorology, we will need to directionally quantify how mixing heights and winds might influence concentrations. Since we noted that the existing upper-air meteorology sites were of only limited use, out estimates of mixing heights in the central basin will have high ranges of uncertainty. Nevertheless, they will serve to help understand the influence of meteorology on concentrations.

## 5.6 Schedule

A draft report summarizing the results of phase II will be submitted to NREL and CRC by April 30, 2001. A final phase I report will follow receipt of comments by approximately one month.

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